

SCIENCE FOR CERAMIC PRODUCTION

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MODIFYING EFFECT OF MICROADDITIVES IN SILICATE AND OXIDE CERAMIC MATERIALS

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The results of studying the modifying effect of small additives on the synthesis, sintering structure, and properties of crystalline phases of ceramic materials in the $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system and other oxide systems are summarized. The structural-energy criteria for evaluation and prediction of the effect of additives are proposed. Examples of practical use of the preliminary prediction of the modifying effect of additives in silicate and oxide systems in the production of ceramics and ceramic pigments are given.

Domestic (A. S. Berezhnoi, P. P. Budnikov, N. M. Pavlushkin, D. I. Poluboyarinov, S. G. Tresvyatskii at al.) and foreign scientists in 1960–1980s investigated the effect of small quantities (0.5–5.5 mol.%) of additives on synthesis and sintering of crystalline phases in oxide systems. The published results were sometimes contradictory and did not make it possible to deduce a general pattern.

In researching modification of ceramics materials in the $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system using additives, we discovered a difference between the effect of microadditives (0.1–1.0 mol.%) and macroadditives (1.0–10.0 mol.% and more) in oxide systems [1–6].

It was found that microquantities of additives in most cases are more effective than the same materials in macroquantities and, moreover, microadditives have an effect not only in simple oxide systems (anion O^{2-}) but also in silicates characterized by complex anion groups from $[\text{SiO}_4]^{4-}$ to $[\text{Si}_x\text{O}_y]^{z-}$ that are formed as the result of polymerization of $[\text{SiO}_4]^{4-}$ tetrahedra in one, two, or three directions (USSR Inventor's Certif. No. 392044) [1–9]. This made it possible to develop a number of compositions and production methods for ceramics with crystalline phases of the $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system (USSR Inventor's Certif. Nos. 392044, 501051, 607826, and 1353787).

The study of modification of the phases of the $\text{MgO} - \text{Al}_2\text{O}_3$ systems by microadditives revealed certain regularities of the effectiveness of additives depending on the ratio of the cation radius of the additive to the modified oxide and on the difference between the electronegativity of the additive and the modifying oxide atoms (Table 1).

We finally proposed a method for qualitative evaluation and prediction of the effect of additives using diagrams that take into account the specified parameters (Fig. 1).

The main evaluation criteria were the difference in electronegativity, the difference in the cation radius, and the value of the cation bond with oxygen in the modified compound. The graphic evaluation form presented in the diagrams in the coordinates “electronegativity difference – relative difference in cation radii” was found to be acceptable. The electronegativity difference is measured according to Mulliken and the difference is taken as the absolute value.

In constructing such diagrams, it has been found (Fig. 1) that the points characterizing cations of effective additives are predominantly localized in that zone of the diagram, where the electronegativity differences approach the force of a single $\text{Me} - \text{O}$ bond in the modified oxide. Hence the factor that indirectly characterizes the degree of delocalization of electrons in microvolumes of the material under the effect of additives is the difference in electronegativities of the cations. As the difference in electronegativity of the cations approaches the force of a single $\text{Me} - \text{O}$ bond, the bond of oxygen either with the additive cation or with the sintering oxide cation is weakened, which, in turn, weakens the bonds between the particles, microcrystals, and blocks (i.e., at the sites where additives are localized). This intensifies the process of consolidation of disperse oxides under the effect of surface tension forces via the mechanism of boundary sliding of grains at the initial stages of sintering. In this case, the process of boundary diffusion of grains at the final stages should be more intense. Partial dissolution of additives in the lattice of sintering oxides activates the process of volume diffusion, which is corroborated by a decrease in the activation

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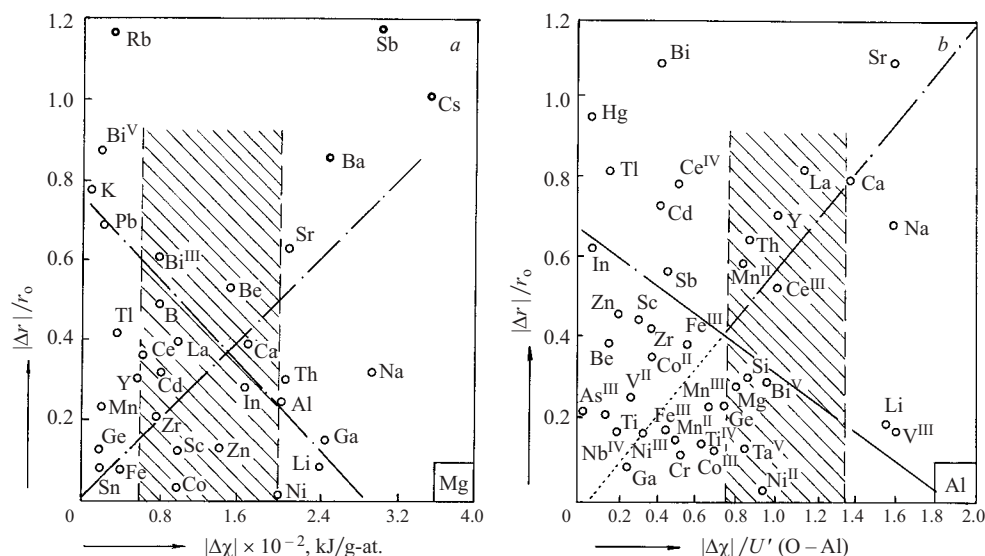


Fig. 1. Diagram of preliminary evaluation of the mechanism of modifiers effect and their efficiency in magnesium systems (a) and in aluminum oxide and aluminosilicate (b): $|\Delta r|/r_0$ relative difference in ionic radii.

energy under the effect of additives both in the initial and in the final stages of sintering.

A verification of the proposed method of evaluation of the modifying effect of additives on other oxide systems confirmed the efficiency of additives Ca^{2+} , Mn^{2+} , Y^{2+} , and Cr^{2+} in zirconium dioxide ZrO_2 and additives Ca , Mn^{4+} , Cu^{2+} , and V^{3+} in tin dioxide SnO_2 . The additives of Be^{2+} , Ce^{4+} and Ta^{5+} are predicted to be effective for sintering of Y_2O_3 . That is how the type of reaction of an additive with a modified oxide is evaluated according to the Tresvyatskii – Lopato diagram. As the difference in the cation radii grows, the solubility of the additive decreases and the chemical reactions intensify.

The proposed graphic method makes it possible to estimate the effect of additives in silicate minerals as well, taking into account the specifics of the structural pattern of their silicon-oxygen skeleton.

All the most effective modifiers of close-grained protoenstatite MgSiO_3 on the diagram constructed for magnesium system are arranged in the upper sector of the diagram (Fig. 1a), where the relative difference of the cation radii exceeds 0.45 (45%). The modifiers of the coarse-grained clinoenstatite modification of MgSiO_3 , on the contrary, are localized in the lower sector of the diagram, whereas atoms of inert additives or weak modifiers of protoenstatite occupy the lateral sectors of the diagram. The modifiers of close-grained forsterite are found in the sector with the relative radius difference ranging from 0.25 to 0.35, which correlates with the limited solubility of the additives. An additional factor for these additives is the high melting point of silicate compounds.

The linear dependences of the concentrations of modifying microadditives on the cation radius and the product of the

TABLE 1

Phase of system	Physicochemical process	Temperature interval, °C	Additives		Range of atomic content of effective additives	Type of dependence
			inert and passivating	activating		
$\gamma\text{-Al}_2\text{O}_3$ $\chi\text{-Al}_2\text{O}_3$	Formation of $\alpha\text{-Al}_2\text{O}_3$	950 – 1300	Ni, Be, B, Se, Ce, Br, Th, Co	V, Mn, Mo, La, Co, Mg, Zn, Zr, Cr	0.10 – 1.00	Intensification of effect with a decreasing difference in the cation radii of the additive and Al
$\text{MgO} + \text{Al}_2\text{O}_3$	Synthesis of MgAl_2O_4	950 – 1400	B, Zr, Ba	Be, Sr, Se, Y, La, Hf, Th	0.10 – 0.80	Intensification of effect with decrease in the product of the radius by the ion charge in additive groups
$\alpha\text{-Al}_2\text{O}_3$	Mineralization of $\alpha\text{-Al}_2\text{O}_3$ and sintering	1300 – 1700	Sr, B, Zr	Mg, Y, Cr, Mn	0.25 – 0.75	Dependence of effect on electro-negativity difference $\Delta\chi$, energy of oxygen bond, and $\Delta\chi$ of cations of additive and modified oxide
MgO	Sintering	1100 – 1500	Ba, Ni, Fe	Be, Sr, Se, Y, La, Ca, Zr, Ce, Th	0.10 – 0.20	
MgAl_2O_3	The same	1300 – 1550	Zr, Ca, Ba	Be, Sr, Y	0.09 – 0.80	

Period	Subgroup																	
	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIIIa	Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	VIIIb		
1	(H)																	
2	<div><div><div></div></div>1+ Li 0.68</div>	<div><div><div></div></div>2+ Be 0.34</div>	<div><div><div></div></div>Modifiers of clinoform MgSiO₃ (large crystals)</div>										<div><div><div></div></div>3+ B (0.20)</div>	<div><div><div></div></div>4+ C</div>	<div><div><div></div></div>3+ N</div>	<div><div><div></div></div>3+ O</div>	<div><div><div></div></div>3+ F</div>	<div><div><div></div></div>3+ Ne</div>
3	<div><div><div></div></div>1+ Na 0.98</div>	<div><div><div></div></div>2+ Mg 0.74</div>	<div><div><div></div></div>Modifiers of protoform MgSiO₃ (fine crystals)</div>										<div><div><div></div></div>3+ Al 0.67</div>	<div><div><div></div></div>4+ Si 0.39</div>	<div><div><div></div></div>3+ P</div>	<div><div><div></div></div>3+ S</div>	<div><div><div></div></div>3+ Cl</div>	<div><div><div></div></div>3+ Ar</div>
4	<div><div><div></div></div>1+ K 1.83</div>	<div><div><div></div></div>2+ Ca 1.04</div>	<div><div><div></div></div>3+ Sc 0.83</div>	<div><div><div></div></div>4+ Ti 0.64</div>	V	<div><div><div></div></div>3+ Cr 0.64</div>	<div><div><div></div></div>2+ Mn 0.91</div>	<div><div><div></div></div>2+ Fe 0.80</div>	<div><div><div></div></div>2+ Co 0.78</div>	<div><div><div></div></div>2+ Ni 0.74</div>	Cu	<div><div><div></div></div>2+ Zn 0.83</div>	<div><div><div></div></div>3+ Ga 0.62</div>	<div><div><div></div></div>4+ Ge 0.44</div>	<div><div><div></div></div>3+ As 0.69</div>	<div><div><div></div></div>3+ Se</div>	<div><div><div></div></div>3+ Br</div>	<div><div><div></div></div>3+ Kr</div>
5	<div><div><div></div></div>1+ Rb 1.49</div>	<div><div><div></div></div>2+ Sr 1.20</div>	<div><div><div></div></div>3+ Y 0.97</div>	<div><div><div></div></div>4+ Zr 0.82</div>	Nb	Mo	Tc	Ru	Rh	Pd	Ag	<div><div><div></div></div>2+ Cd 0.99</div>	<div><div><div></div></div>3+ In 0.92</div>	<div><div><div></div></div>2+ Sn 0.67</div>	<div><div><div></div></div>3+ Sb 0.90</div>	<div><div><div></div></div>3+ Te</div>	<div><div><div></div></div>3+ I</div>	<div><div><div></div></div>3+ Xe</div>
6	<div><div><div></div></div>1+ Cs 1.65</div>	<div><div><div></div></div>2+ Ba 1.38</div>	<div><div><div></div></div>3+ La 1.04</div>	Hf	Ta	W	Re	Os	Ir	Pt	Au	<div><div><div></div></div>2+ Hg 2.11</div>	<div><div><div></div></div>3+ Tl 1.05</div>	<div><div><div></div></div>2+ Pb 1.26</div>	<div><div><div></div></div>3+ Bi 1.20</div>	Po	At	Rn
7	Fr	Ra	Ac	Ku														
			<div><div><div></div></div>(3+) Ce 1.02</div>	Lanthanides														
			<div><div><div></div></div>4+ Th 0.95</div>	Actinides														

Fig. 2. Position of modifiers of coarse-crystalline clinoenstatite and fine-crystalline protoenstatite in the Mendeleev Periodic Table (based on experimental data).

radius by the charge for the oxides in the $\text{MgO} - \text{Al}_2\text{O}_3$ system (Fig. 2) made it possible to propose a structural-energy coefficient for comparative evaluation of the efficiency of additives belonging to the same subgroup of the Mendeleev Periodic Table, which includes the ratio of the free energy values of oxide formation converted to one atom (the thermodynamic criterion) and the relative difference in the ionic radii (the crystal-chemical criterion):

$$K_{\text{ef}} = \frac{\Delta F_g^1 / \Delta F_o^1}{|\Delta r|/r_o},$$

where K_{ef} is the structure-energy coefficient of the effectiveness of the modifying oxide in a particular material; ΔF_g^1 and ΔF_o^1 are the values of the free energy of oxide formation of the additive and the main material converted to one atom; $|\Delta r|/r_o$ is the relative difference of the crystal-chemical radii of the additive and sintering oxide cations.

At the same time

$$\Delta F^1 = \frac{\Delta F}{mZr},$$

where ΔF is the free energy of oxide formation (Helmholtz energy); m is the number of metal atoms in the oxide formula; Z and r are the charge and radius of the cation.

A condition for using the proposed coefficient is the inequality $|\Delta r| \neq 0$.

The calculated values of K_{ef} agree well with the experimental data and confirm the experimental dependences of

the effect decreasing with increasing cation radius in groups of similar additives.

This method was used in searching for effective additives to obtain ferrites in the $\text{ZnO} - \text{MnO} - \text{Fe}_2\text{O}_3$ system. Using this method, the modifiers for polymorphic phases of magnesium metasilicate, namely, close-grained protoform of MgSiO_3 and coarse-grained clinoform of MgSiO_3 , have been selected.

Modification of close-grained protoenstatite provides for the production of high-strength stable non-aging steatite ceramics. The amount of additive introduced to modify the protoform of MgSiO_3 is calculated according to the mechanism proposed. Thus, in modifying MgSiO_3 produced by thermal decomposition of talc or crystallization of a stoichiometric melt using microadditives, the effect of thermochemical dispersion of pyroxene was registered, which is as follows. If cations whose crystal-chemical radius differs by more than 50% from the central cation radius are uniformly introduced into pyroxenes, the large crystals under firing disintegrate to a size of 0.5 – 1.0 μm , i.e., to the limiting size below which the material transforms into an x-ray-amorphous state. According to the proposed model, cations of such additives incorporating into the crystal lattice of pyroxene break long pyroxene chains into short fragments.

The increase in the system energy due to its dispersion is compensated by the decrease in the lattice energy and the specific interphase energy of crystals modified by microadditives. The perfection of the crystalline lattice of MgSiO_3 and the formation of a rounded shape in microcrystals coated by a silicate melt (glass) have been established experimentally.

TABLE 2

Modifying oxide	Boundary content of additive in MgSiO ₃ , %		Sizes of microcrystals, μm	
	experimental data	calculated data	experimental data	calculated data
BeO	0.10	0.11	0.5	0.50 – 0.53
SrO	0.11	0.11	0.5	0.49 – 0.51
BaO	0.12	0.12	0.5	0.45 – 0.58

To determine the bounds of the optimum quantities of modifiers to disperse pyroxenes, the following formulas can be used:

$$P_o^1 = \frac{c}{nR} \times 100 \text{ (mol.\%);}$$

$$P_o = \frac{cM_2}{nRM_1} \times 100 \text{ (wt.\%),}$$

where P_o^1 and P_o is the amount of the additive oxide; c is the elementary cell parameter of pyroxene along the axis c ; n is the number of metal atoms in the modifier oxide formula; R is the size of the emerging crystals; M_1 and M_2 is are the molar parts of the pyroxene and the modifying oxide.

The lower concentration bound of the additive dispersing pyroxene is determined by the ratio of the lattice parameters along the axis c and the mean size of dispersed crystals. The experimental and calculated sizes of microcrystals and the boundary contents of modifying additives agree well (Table 2).

The calculated and experimental values of the content of similar modifying oxides for fine-grained pyroxenes are close, which also agrees with the modification model considered. The quantitative effect of additives is expressed in saturation. It is established experimentally that to accelerate the process and for better control of the finely crystalline structure of the product, it is advisable to introduce the additive in an amount an order of magnitude higher than the minimum quantity calculated from the formula

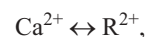
$$5P_o \leq P \leq 10P_o.$$

As the cation radius decreases, the dispersion rate grows and the temperature of the process completion decreases from 1400°C (BaO additive) to 1280°C (BeO additive), which is due to the increased mobility of the cation and a more intense ionic field of Z/r^2 .

The effect of Ce^{4+} , Ti^{4+} , Ti^{4+} , Bi^{3+} , Pb^{2+} , and other additives was predicted based on the proposed model. The effect of thermochemical dispersion has been experimentally confirmed in introducing the respective additives into diopside and spodumene. The model of the mechanism of the modifying effect in the dispersion of pyroxene is confirmed by the formation and stabilization of the protoenstatite modification of MgSiO₃, which has a larger lattice parameter along the c axis than other modifications of MgSiO₃.

The introduction of additives that can isomorphically replace magnesium in crystalline compounds ensures the formation of coarsely crystalline clinopyroxenes (clinoenstatite and diopside) in the products of firing of talc and tremolite.

Taking into account this approach, a technology for tinting disperse MgSiO₃ and CaSiO₃ by boiling in a solution of iron, manganese, cobalt, copper, and nickel salts (USSR Inventor's Certif. No. 1353787) was developed. It was found that ionic exchange in the surface layer of these pyroxene minerals proceeds according to the scheme:



where R^{2+} is used for Co^{2+} , Ni^{2+} , Fe^{2+} , Mn^{2+} , and Cu^{2+} .

The revealed regularities of pyroxene modification were implemented in producing ceramic pigments from natural materials: talc, tremolite, and diopside [7, 8]. The hydrogen ion H^+ (proton) can also be used as a modifier of near-surface oxide layers when its atomic content is below 0.1% [9]. In the context of proton modification of oxides, diaspore, which is a natural aluminum hydroxide (AlO(OH)), can be regarded as protonized α -Al₂O₃, which is confirmed by the formation of α -Al₂O₃ on the basis of diopside at a temperature of 500°C without intermediate forms of Al₂O₃ ($\gamma_1 - \theta_1 - \delta_1$, etc.) [6].

The considered approach to the selection of modifying additives and reactants has lately been successfully implemented [7 – 14] in the development of compositions and technologies for ceramics and other silicates based on technical-grade oxides and natural materials.

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